

# **Relating Ocean Optics to Photochemical Transformations of Dissolved Organic Carbon**

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## **LONG-TERM GOALS**

The long-term goal of this research is to use remotely sensed and *in situ* ocean optical data together with photochemical rate determinations to estimate the spatial and temporal significance of photochemistry to marine organic carbon transformations and optical changes resulting from these processes.

## **OBJECTIVES**

The central objective of this research program has been to examine quantitatively the links between optical measurements and photochemical carbon transformations in the sea. Our goal is to establish quantitative methods to relate variability in water-leaving radiance to photochemical reactions that lead to direct loss of colored dissolved organic matter (CDOM) and consequent changes in UV optical properties in the photic zone. We hope to establish bounds for spatial and temporal variability in the spectral efficiency of CDOM fading for use in numerical models that predict the time course of change for the UV and blue spectral regions of radiation in the surface ocean.

## **APPROACH**

To achieve the objectives stated above requires a wavelength dependent description of the *in situ* optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of CDOM. Our general approach uses three connected principles:

- (1) Previous ONR work indicates that there are strong relationships between water-leaving radiance in the visible (412 nm) and diffuse attenuation of UV radiation (323 nm, 338 nm, and 380 nm) (Johannessen et al., 2002).
- (2) CDOM is the dominant contributor to the absorption and attenuation of UV in coastal waters and diffuse attenuation of UV can be related directly to its absorption (Johannessen et al., 2002).
- (3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores (i.e. CDOM fading) and production of lower-molecular weight compounds. Wavelength-dependent apparent quantum yields (AQYs) for these transformations can be determined experimentally.

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Given measurements of solar radiation and upwelling radiance at the sea-surface, we estimate photochemical losses of surface-layer CDOM by applying empirical relationships between: (1) reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) that simultaneously measures incident irradiance ( $E_d$ ) and upwelling radiance ( $L_u$ ) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) that measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II, chlorophyll fluorescence (WETStar miniature flow through fluorometer), conductivity, and temperature. Both instruments are deployed simultaneously to accumulate UV/VIS optical data ( $E_d$ ,  $L_u$ , &  $K_d$ ) while collecting discrete rosette samples at the same station for evaluation of CDOM absorption.

Laboratory irradiations (both on shore and at sea) are used to quantify the efficiency of CDOM driven photochemical processes. Using a broad-spectrum 1.5 kW xenon lamp, a series of sequential long-pass optical filters, and a statistical evaluation (Rundel, 1983) of the resulting photochemical rates in 15 quartz containers, we calculate the AQY spectrum for photochemical consequences (ex. fading,  $\text{CO}_2$  production) of CDOM reactions with a single irradiation experiment. This represents a novel approach to photochemical AQY determinations that is much faster than other monochromatic approaches (3 hrs vs. 3 weeks in some cases). This allows evaluation of both spatial and temporal variations in AQY spectra, not previously possible with other approaches. By combining spectral photochemical efficiency data, absorbance data, attenuation profiles, and solar spectral irradiance, we can calculate both whole water column and depth discriminated photochemistry.

Relationships developed using TSRB-II and SPMR data combined with discrete measurements of CDOM absorbance, allow us to combine remotely sensed data with irradiance and water optical models to estimate the photomineralization of CDOM in the coastal ocean. These data represent the beginning of regional photochemical inventories and a starting point for long-term regional scale studies of photochemical carbon transformations in the coastal ocean.

At Dalhousie, Bill Miller (PI), Lori Ziolkowski (technician), and a graduate student, Cedric Fichot, (M.Sc.), have the ONR project as their primary effort. An undergraduate (Catherine Garagon) was employed part-time for computer programming. Our field optical component benefits greatly collaboration with J.J. Cullen's group (w/ R. Davis) and assistance from Satlantic, Inc. (instrument development, optical expertise, field and computer assistance). This year, our field collaborations were with Drs. R. Powell (LUMCON) and W. Landing (Florida State University) on a cruise to the Gulf of Mexico (3 of 3 planned) and with D. Kieber (SUNY-Syracuse) and K. Mopper (NSF funding) for a cruise in the Gulf of Maine and the N.W. Atlantic (2 of 3 planned). This later cruise marks the first field effort of a new collaboration with L. Martin-Traykovski and H. Sosik (WHOI: NOAA funding) to examine methods for assigning varying photochemical efficiency spectra for  $\text{CO}_2$  production to proper water types using satellite optical data. We also used the opportunity of participation in a 28 day iron addition experiment (part of the Canadian SOLAS Network) to collect additional optical data relevant to our ONR objectives.

## WORK COMPLETED

We staged for and participated in three research cruises: N.W. Atlantic, Subarctic Pacific, and the Gulf of Mexico (above). These efforts included successful completion of both laboratory irradiations and collection of *in situ* optical data.

We developed and constructed a second version of the sequential long band-pass filter irradiation box with greater temperature control during irradiation, an improvement required to study photochemical rates at lower temperatures found in higher latitude study areas.

We continued examination of variations in photochemical efficiency surfaces for CDOM fading.

We significantly modified MATLAB® code for more efficient calculation of AQY spectra and CDOM fading surfaces from experimental irradiation data including Graphical User Interfaces (GUIs).

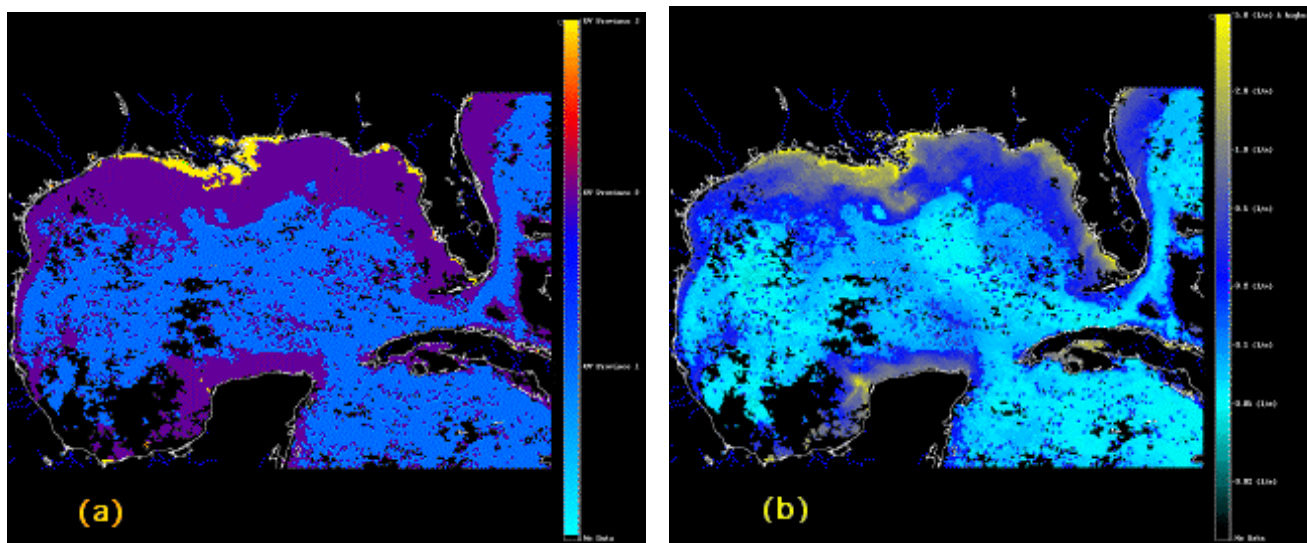
We made major changes to our surface ocean mixed layer model that calculates CDOM fading, increasing efficiency, accuracy, and running speed. Added GUI to mixing model.

We developed a new approach and new algorithms for relating  $K_d$  in the UV to visible satellite reflectance, allowing us to match water types with more accurate mathematical  $K_d$  descriptions.

We have not submitted data to a national archive.

## RESULTS

We have continued to accumulate samples and optical data from diverse water types in an effort to build robust optical relationships that will be useful in predicting photochemistry from remotely sensed data. This year, we added new data from the Gulf of Maine, N.W. Atlantic, the Gulf of Mexico, and the subarctic Pacific. Using data amassed since the start of our ONR contract, we have modified our approach for relating  $K_d$ s in the UV to satellite reflectance ratios ( $Lu_{x/y}$ ). Instead of using a single  $Lu$  ratio (412nm/555nm) as we have in the past, three specific ratios and ratio combinations were identified that allow empirical grouping of optical signals into 3 data subsets (referred to as UV provinces in Figure 1(a)) with specific fitting functions tailored to each subset. Using this approach, we have improved accuracy of  $K_{dUV}$  estimates for coastal waters from remotely sensed ocean color in the visible. Also, by applying nonlinear fitting functions to our *in situ*  $K_d$  data sets at all 14 wavelengths for interpolation, we now have developed relationships between  $Lu_{VIS}$  for all UV wavelengths (instead of only those wavelengths measured by our profiler). As part of his thesis research, Cedric Fichot worked on this new approach and we can now routinely produce regional maps of  $K_{dUV}$  from SeaWiFS data (Gulf of Mexico used as example, Figure 1(b)). This is a major step forward in evaluating CDOM photochemical rates over larger scales than can be achieved using cruise data alone.

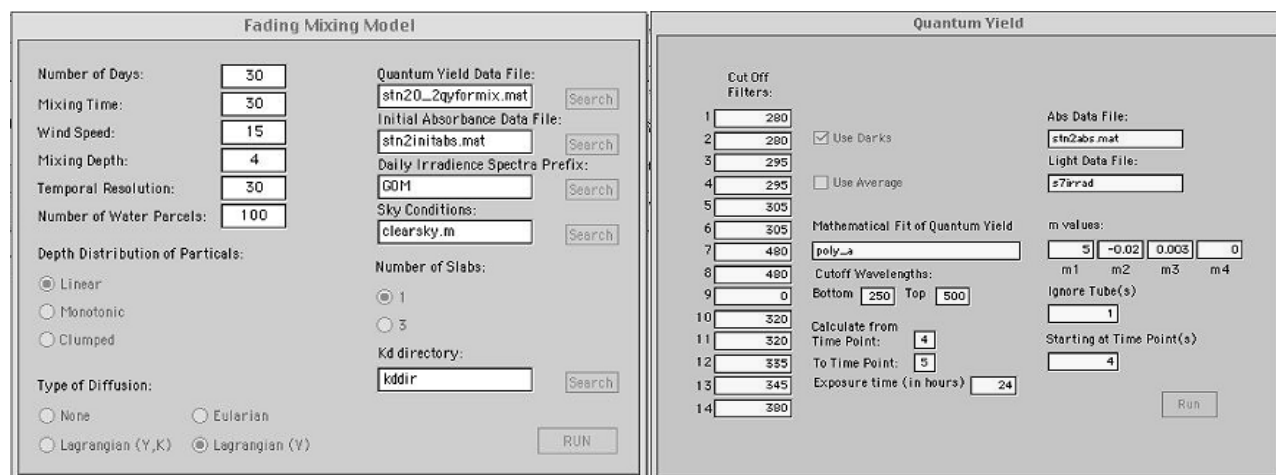


**Figure 1. Gulf of Mexico mapped for (a) UV provinces and (b) total attenuation at 350nm.** [Two colour pictures generated from a SeaWiFS satellite image that show (a) UV provinces as yellow, purple, and blue and (b) calculated total attenuation at 350nm as a continuum from light blue to yellow. Attenuation shows highest values around the Mississippi river outflow and in coastal regions, capturing mixing fixtures and in coastal and open ocean locations throughout the Gulf.]

Further development of MATLAB® code has achieved more flexible application of fitting functions to our quantum efficiency calculations. We have cleaned up redundant code, updated our programs with more efficient statistical treatments, and made to entire process more “user-friendly” by developing flexible Graphical User Interfaces (GUIs: screen shots shown in Figure 2 below). Our continued work on defining the 3-diminsional efficiency surfaces for CDOM fading has produced confidence in results (uncovering a few previous programming errors which have been corrected). Quite a lot of time has been spent to produce clean and efficient code, reducing run-times for our surface ocean fading model (reported last year) by more than a factor of ten.

## IMPACT / APPLICATIONS

The optical properties of CDOM in the ocean control photochemical rates, effect oceanic chemical cycles, and influence the interpretation of ocean color (Miller, 1998). We feel that instrumentation capable of characterizing UV radiation in the surface ocean together with new algorithms allowing estimation of UV attenuation from satellite data will prove invaluable to the understanding of the variability in the CDOM signal. Our approach to linking CDOM photochemical models to V radiation is similar enough to field observations to argue that additional effort will produce a critical component toward predictive capability for CDOM dynamics. While a large effort is still needed on both optical and photochemical research fronts, the approach developed thus far appears to be sound and should lead to novel and critical insight on the link between ocean optics and photochemical carbon transformations. It will also result in the unique ability to address the regional and global significance of photochemical reactions in the ocean.



**Figure 2. Computer Screen Shots of new Graphical User Interface (GUIs)**  
*[Two computer screens developed in Matlab to allow easy input of model parameters for both our mixed layer fading model (left) and our AQY calculations (right). Entry fields are provided for required details such as data file location, mixed layer depth, wind speed, irradiance data, time-step, and model runtime in the mixed layer fading model (left) and the location of specific optical cutoff filters relative to quartz sample tubes, tube-specific irradiance and absorbance data file location, initial model parameters and mathematical fitting function used in our AQY calculations]*

## TRANSITIONS

We continue to receive offers to participate with several groups interested in other photochemical processes due to the ONR sponsored development of UV sensors and multispectral approaches to AQY determinations. This will continue to produce opportunities to add varied water types to our expanding optical database and provide samples for photochemical evaluation. Development of new MATLAB® algorithms (by Cedric Ficot and Lori Ziolkowski in collaboration with J.J. Cullen and R. Davis) will provide novel tools to expand quantitative evaluations of photochemistry to new groups in marine chemistry. These numerical approaches relieve many of the time constraints previously present in photochemical studies and will make spatial and temporal evaluation of CDOM dynamics feasible.

## RELATED PROJECTS

At Dalhousie, Bill Miller (PI), Lori Ziolkowski (technician), and a graduate student, Cedric Fichot, (M.Sc.), have the ONR project as their primary effort. Our field optical component benefits greatly collaboration with J.J. Cullen's group (w/ R. Davis) and assistance from Satlantic, Inc. (instrument development, optical expertise, field and computer assistance). Development of novel optical instrumentation along with J.J. Cullen efforts on optical models, data analysis, and instrument development are closely related to this project. The timely development of both our novel Satlantic instruments and numerical modeling approaches benefits from these relationships. As stated above, we have collaborated with four groups on three cruises to obtain optical data, photochemical data, and the numerical relationships connecting the two. In each case, we continue to use cruises of opportunity

(only one funded for shipping and travel by ONR) to expand our observations and experimental data integral in our ONR objectives. Our funding to participate in all but the SOLAS cruise is limited to shipping and travel costs since NSF and NOAA do not support Canadian collaborators beyond this amount. Leverage of Canadian funding of photochemical projects, however, can be used to allow expanded optical measurements that greatly benefit our ONR program.

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